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An alternative method to determine the share of fossil carbon in solid refuse-derived fuels – Validation and comparison with three standardized methods

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ABSTRACT

Today different types of wastes are used as refuse-derived fuels (RDF) either in waste-to-energy plants or as fuel substitutes in energy-intensive industrial processes. In order to quantify their greenhouse-gas relevance (fossil carbon content), reliable and practical analytical methods are required, which allow differentiation between biogenic and fossil organic carbon. In the present paper, an alternative method to determine the fossil share in RDFs is examined and validated. The so-called "adapted Balance Method" (aBM) is applied to three different RDFs and the results are compared to three standardized methods, namely the Radiocarbon Method (^{14}C-Method), the Selective Dissolution Method (SDM), and the Manual Sorting Method (MS). The aBM is based on the distinctly different elemental composition of water-and-ash-free biogenic and of fossil matter (TOX_{BIO} and TOX_{FOS}). Within the study, these compositional data are derived by manual sorting of the RDFs. The results show that the values obtained by the aBM are in excellent agreement with the results of the ^{14}C-Method (considered as reference method). Mean deviations between the two methods of −0.9 to +1.9% absolute for the share of fossil carbon are found which are statistically insignificant. High trueness and reliability of the aBM can be expected, independent of the RDF type. In contrast, the reliability of the other standardized methods (SDM and MS) appears to strongly depend on the type and composition of the RDF. The results further indicate that the generation of RDF-specific data on TOX_{FOS} is important for the aBM if significant shares of polymers with comparably high oxygen content might be present in the RDF and if low uncertainties of the results (<3% relative) are required. The findings demonstrate that the alternative method has advantages compared to standardized methods with respect to reliability and/or costs.

1. Introduction

The utilization of waste materials as a secondary energy resource is increasing throughout most of the world. Today many wastes and waste fractions are used for energetic applications, a practice supported by national governments and the European Commission [1]. Policies on waste management and emission reductions as well as on the energy market have been established. The implementation of the Kyoto-protocol further stimulates the use of biomass-containing alternative fuels (e.g. Renewable Energy Directive [2], Directive on greenhouse gas emission trading [3], Landfill Directive [4], Chinas national emission trading System [5], Egyptian coal regulations [6]). Refuse-derived fuels (RDF) are being used in both, waste-to-energy plants and as a fuel substitute in energy-intensive industries. RDF in industrial processes are

Abbreviations: A, ash content; aBM, adapted Balance Method; BM, Balance Method; C&I, commercial & industrial waste; MS, Manual Sorting method; MSW, municipal solid waste; n, number of samples; RDF, refuse-derived fuel; R^2, correlation coefficient; SD, standard deviation; SDM, Selective Dissolution Method; SRF, solid recovered fuel; *TC*, total carbon in the water-free sample; TH, total hydrogen in the water-free sample; TIX_{wf}, total inorganic content of the respective element in the water-free ash; TN, total nitrogen in water-free sample; *TO*, total oxygen in the water-free sample; *TOC*, total organic carbon; *TOH*, total organic hydrogen; *TON*, total organic nitrogen; *TOO*, total organic oxygen; *TOS*, total organic sulphur; TOX_{BIO}, total organic content of the respective element in the water-and-ash-free biogenic matter; TOX_{FOS}, total organic content of the respective element in the water-and-ash-free fossil matter; TOX_{RDF}, total organic content of the respective element in the water-and-ash-free RDF; TS, total sulphur in the water-free sample; TX_{wf}, total content of the respective element in the water-free sample; waf, water-and-ash-free; wf, water-free; wt%, percentage by weight; $x_{B,waf}$, biogenic mass fraction on water-and-ash-free basis; $x_{B,wf}$, biogenic mass fraction on water-free basis; $x_{B,TC}$, share of biogenic carbon; $x_{F,waf}$, fossil mass fraction on water-and-ash-free basis; $x_{F,wf}$, fossil mass fraction on water-free basis; $x_{F,TC}$, share of fossil carbon; ^{14}C-Method, Radiocarbon Method; %abs, absolute percentage; %rel, relative percentage

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utilized to save costs for fuels, to reduce natural resource consumption and to lower the amount of greenhouse gas emissions associated with the production process [7–9]. Due to the CO_2 emission trading scheme in place in Europe [10], lowering fossil CO_2 emissions by utilizing biomass-containing RDFs is of economic relevance for cement manufacturers. CO_2 emissions stemming from the biogenic matter are regarded as carbon neutral, whereas CO_2 from fossil matter is climate-relevant.

The prime example for the utilization of RDFs is the cement industry, which represents one of the most material-, energy-, and CO_2-intensive industries [11,12]. Within the European Union, more than 34% of thermal energy demand in the production process of cement plants is already provided by RDFs [13]. In some European countries the substitution rate of primary energy carriers has already reached a level of above 50% – e.g. Austria 76.1% (2015) [13], Germany 64.6% (2015) [14], Belgium 60% (2011) [15], Switzerland 53.7% (2014) [16].

Compared to fossil fuels, RDFs exhibit a much broader variation in composition, which strongly depends on the waste utilized for RDF production. Variations can easily appear due to different types of commercial and industrial waste, municipal solid waste, waste collection scheme, or seasonal variations in waste generation. In order to check the quality of solid RDFs with respect to their composition (e.g. calorific value, biomass content, heavy metal contents) and their associated environmental impacts, reliable and practical methods are required. Both, waste management companies generating RDFs and industries utilizing these fuels require tools for reporting and documentation purposes. With respect to the determination of the climate-relevant share in solid RDFs, three methods are described in the standard EN 15440:2011: the Manual Sorting method (MS), the Selective Dissolution Method (SDM), and the Radiocarbon Method (^{14}C-Method) [17]. Furthermore, the Balance Method (BM) has recently been published in the Standard ISO 18466:2016 [18] and has also been recognized by the United Nations Framework Convention on Climate Change (UNFCC) as an approved methodology to determine the fraction of fossil carbon in waste [19]. Table 1 summarizes the available methods with respect to their applicability to solid RDF samples ("prior combustion") and/or to gaseous samples ("post-combustion"). Possible outcomes (parameter) of the methods are listed.

Only the BM and ^{14}C-Method are applicable for a "post-combustion" analysis in the flue gas, whose representative sampling is considerably easier compared to the solid waste material, as the latter is much more heterogeneous. The BM is able to monitor the fossil share in the input of waste-to-energy plants in real-time [20–22]. This is possible by using operating data of the waste-to-energy plant, usually making additional sampling and analysis campaigns redundant. Yet, characterizing the waste and RDFs *prior* to combustion requires solid samples to be analyzed. This is possible by means of the MS, SDM, and ^{14}C-Method and by means of a recently adapted version of the BM (adapted Balance Method). The adapted Balance Method (aBM), which relies on the analysis of the elementary composition of the RDF in the laboratory, has recently been successfully applied to artificially produced RDFs [23,24]. Some methodological and economic benefits compared to the laboratory-based standardized methods (SDM, MS, ^{14}C-Method) have been identified so far; i.a.:

- In contrast to SDM and MS, the uncertainties of the aBM results are statistically derived. They are propagated from the uncertainties of the input parameters [24]. By comparison, the methodological constraints of the SDM (unselective dissolution) can lead to significant inaccuracies which are difficult to detect and quantify [1,25]. As MS is greatly affected by the knowledge of the sorting person and available facts about the waste compounds, the uncertainties of this method can hardly be calculated [26,27]. Despite the high analytical precision of the ^{14}C-Method, uncertainties for this method are introduced by the choice of a ^{14}C-reference value [28,29].
- The aBM is far less time- and cost-intensive than MS or the ^{14}C-Method. The ^{14}C-Method can only be employed by a limited number of laboratories which are equipped with the appropriate instruments (around 64 laboratories in Europe) [30]. Costs for aBM and SDM are expected in a similarly lower range than MS and ^{14}C-Method [24,30].
- High trueness and precision of the aBM was found recently when defined mixtures of biogenic (e.g. cardboard, paper) and fossil materials (plastics) were investigated (deviations from the theoretical value below 4.5%rel; precision of ±3%rel) [23]. This is better than reported for SDM and MS [27,31,32].
- Contrary to most standardized methods, the aBM can provide a range of parameters with reference to the fossil/biogenic content in RDFs, including the key parameters identified in Table 1. Different parameters may be required depending on the interested party (RDF producer, RDF user, authority, etc.) or the reporting obligations (CO_2-emissions, energy produced, etc.). Thus, when choosing a method one needs to be aware of the potential parametrical limitations of these methods. For example, the ^{14}C-Method does not provide information on the biogenic or fossil mass share in the RDF, whereas from sorting (MS) the share of fossil carbon cannot directly be derived. After sorting, additional information or analyses on the carbon content of the different RDF compounds are necessary. The same applies also to the share of biogenic energy, which is only directly derivable from aBM results.

Table 1
Available methods to determine the fossil share in solid refuse-derived fuels; indicating possible output parameter of the methods and the applicability prior to combustion or as a post-combustion method (measurement in the flue gas).

Method applicable	Parameter			
	Fossil/biogenic **mass** share in wt%	Fossil/biogenic - share of **carbon** in wt% - share of **CO_2-emissions** in wt% - CO_2-emission factor	Ratio of **energy** from fossil/biogenic sources in %	**Plastic** content in wt%
prior-combustion	MS, SDM, aBM	(MS)[3], SDM[1], ^{14}C-Method[2], aBM	(MS)[3], SDM[1], ^{14}C-Method[2], aBM	MS, SDM, aBM
post-combustion	BM	^{14}C-Method[2], BM	^{14}C-Method[2], BM	BM

aBM – adapted Balance Method, BM – Balance Method (ISO 18466:2016), SDM – Selective Dissolution Method (EN 15440:2011), MS – Manual Sorting (EN 15440:2011), ^{14}C-Method – Radiocarbon Method (EN 15440:2011).

[1] SDM: Carbon/energy-based parameters (share of carbon, CO_2-emission factors, ratio of energy) can only be derived when the carbon/energy content is known in the RDF and in the dissolution residue.

[2] ^{14}C-Method: Energy-based parameters (ratio of energy, energy-related CO_2-emission factor) can only be derived when the energy content is known in the fossil and biogenic matter.

[3] MS: Carbon/energy-based parameters (share of carbon, CO_2-emission factors, ratio of energy) can only be derived when the carbon/energy content is known in the fossil and biogenic matter in each compound.

Finally, during a recent interlaboratory comparison, the SDM was applied to determine the ratio of biogenic carbon in RDF samples (output of mechanical biological plant). The results showed that from the values generated by 12 laboratories only 30–70% were within the tolerance limits of two standard deviations [33]. This rather poor result again indicates that routinely applied methods can be unsatisfactory and that the development of alternative approaches is justified.

The objective of the study presented is to examine the aBM as an alternative method for determining the fossil carbon (and mass) share in solid RDFs. Following the promising results with artificially produced

RDFs [23,24], the validation of the method is to be complemented by investigations with real RDF samples. In particular, the study (1) compares results obtained by the aBM with results when standardized methods are applied, (2) appraises the trueness of the aBM results by matching them with ^{14}C-Method analysis results, (3) examines the robustness of the aBM and of the aBM input parameter, and (4) assesses the applicability of the method compared to standardized methods.

To do so, the method is applied to three different RDFs which are drawn from different plants and are produced from different types of waste. The results obtained are compared to results of the standardized methods, particularly the ^{14}C-Method, SDM, and MS, which are all described in EN 15440:2011. The ^{14}C-Method is regarded as the method with the lowest uncertainty when determining the fossil content in mixed wastes and is used as reference method within this study.

2. Materials and methods

2.1. Adapted Balance Method (aBM)

The aBM relies on the distinctly different elemental composition of biogenic and fossil organic matter on a water-and-ash-free basis (where fossil is understood as materials produced out of crude oil, natural gas or coal).

The necessary input data for the aBM comprise:

(1) data on the chemical composition of the water-and-ash-free RDF (TOX_{RDF}) under investigation (example shown in Fig. 1 – bar chart on the right side). These data are derived from elemental analyses together with ash content determination.
(2) data on the elemental composition of the water-and-ash-free biogenic and fossil organic matter present in the RDF (TOX_{BIO}, TOX_{FOS}) (examples shown in Fig. 1 – bar charts on the left). These data can be collected from literature or from manual sorting together with elemental analyses and ash content determinations for each sorted compound (applying Eq. (3)).

Uncertainties in TOX_{RDF}, TOX_{BIO}, and TOX_{FOS} are propagated from the elemental analyses (at least triplicate) and ash content determination (duplicate). By means of balance equations TOX_{RDF}, TOX_{BIO}, and TOX_{FOS} are related by the respective mass shares of water-and-ash-free biogenic matter ($\boldsymbol{x_{B,waf}}$) and water-and-ash-free fossil matter ($\boldsymbol{x_{F,waf}}$). $\boldsymbol{x_{B,waf}}$ and $\boldsymbol{x_{F,waf}}$ are the unknown variables to be determined (illustrated in Fig. 1). The aBM sets up mass balance equations for total organic carbon (*TOC*), total organic hydrogen (*TOH*), total organic nitrogen (*TON*), total organic sulfur (*TOS*), and total organic oxygen (*TOO*). Each balance equation contains the two unknown mass shares $\boldsymbol{x_{B,waf}}$ and $\boldsymbol{x_{F,waf}}$. In addition, the sum of $\boldsymbol{x_{B,waf}}$ and $\boldsymbol{x_{F,waf}}$ is per definition equal to 1. The set of six balance equations (for *TOC*, *TOH*, *TON*, *TOS*, *TOO,* sum of $\boldsymbol{x_{B,waf}}$ and $\boldsymbol{x_{F,waf}}$) is overdetermined (more equations than unknowns). A data reconciliation algorithm based on non-linear optimization can be applied to reveal the quantity of the unknown mass fractions (biogenic $\boldsymbol{x_{B,waf}}$, fossil $\boldsymbol{x_{F,waf}}$). During data reconciliation, the uncertainties in TOX_{RDF}, TOX_{BIO}, and TOX_{FOS} are narrowed and the derived values are used to calculate $\boldsymbol{x_{B,waf}}$ and $\boldsymbol{x_{F,waf}}$ including their uncertainties. Algorithm and further details on the aBM are provided in Fellner et al. (2011) [24]. The fossil mass fraction on a dry basis ($\boldsymbol{x_{F,wf}}$) is determined by considering the ash content (*A*) in the RDF:

$$x_{F,wf} = x_{F,waf} * (1-A) \quad (1)$$

whereby $\boldsymbol{x_{F,wf}}$ represents the fossil mass fraction on a dry basis in kg/kg, $\boldsymbol{x_{F,waf}}$ the fossil mass fraction on a water-and-ash free basis in kg/kg and *A* the ash content in kg/kg.

Inserting the results ($\boldsymbol{x_{B,waf}}$ and $\boldsymbol{x_{F,waf}}$) into the *TOC* balance, allows the fraction of fossil carbon as a percentage of the total carbon to be determined ($\boldsymbol{x_{F,TC}}$):

$$x_{F,TC} = ((x_{F,waf} * TOC_{FOS}) * (1-A) + A * TIC) / TC_{RDF,wf} \quad (2)$$

whereby TOC_{FOS} represents the total organic carbon in the water- and ash-free fossil matter in g/kg$_{waf}$ (e.g. from Fig. 1), *TIC* represents the total inorganic carbon in the water-free ash in g/kg$_{wf}$, and $TC_{RDF,wf}$ the total carbon content in the water-free RDF in g/kg$_{wf}$.

If required, the fossil carbon content of the RDF can easily be transferred to fossil carbon dioxide emissions ($CO_{2,fos}$) by considering the respective molar weights (of carbon and of carbon dioxide). In addition to fossil carbon and $CO_{2,fos}$, the ratio of energy originating from biogenic sources can also be derived. To do so, the heating value of the RDF and of the biogenic matter present in the RDF has to be determined via empirical equations (e.g. after Boie, 1957 or Dulong [34,35]) which use the elemental composition of the fuel.

Finally, fossil CO_2-emission factors (*EF*) can be derived, expressing the mass of climate-relevant CO_2 emitted per unit mass or unit energy content of the RDF:

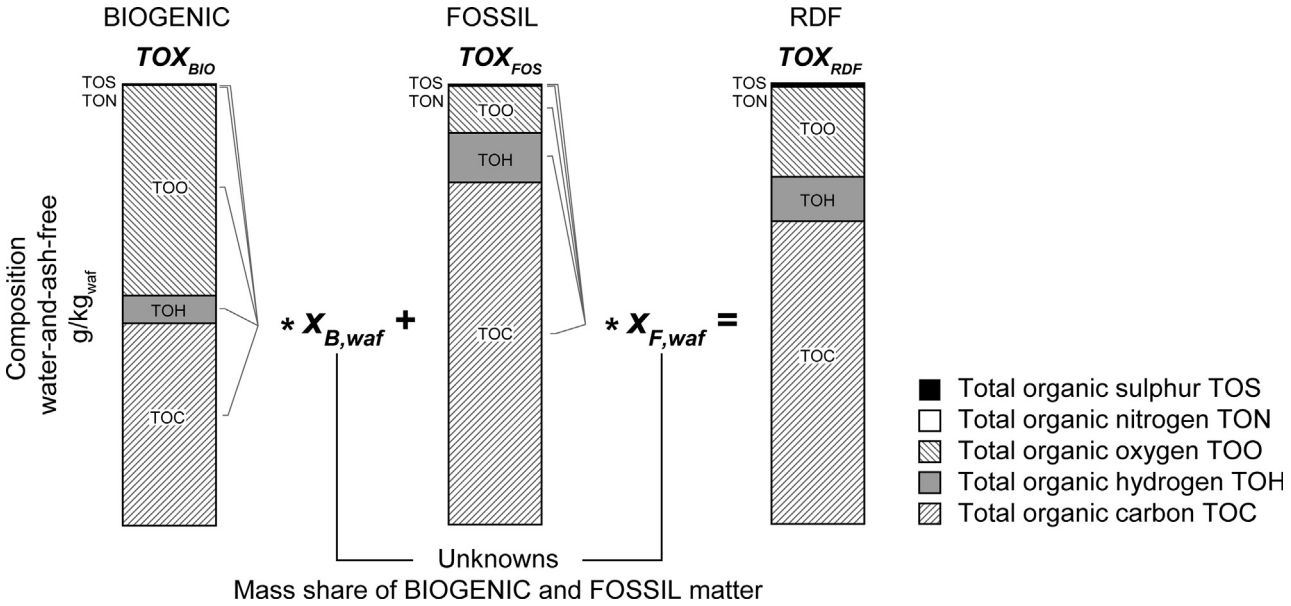

Fig. 1. Schematic illustration of the adapted Balance Method, showing the relation between the elemental composition (on water-and-ash-free reference base) of biogenic organic matter (TOX_{BIO}), fossil organic matter (TOX_{FOS}), and organic matter in the RDF (TOX_{RDF}).

Table 2
Description of refuse-derived fuels investigated and number of samples investigated per method.

	Origin	Remarks on visual appearance	Number of samples investigated[1]			
			^{14}C-Method	aBM	SDM	MS
Paper Reject	Residues discharged after the first process steps of shredding, dissolution, and screening of a recycling paper & board factory	No defined particle size; predominantly cardboard & packaging plastics; partly agglomerated (partly-dissolved cardboard pieces & cellulose fibers attached to plastics); similar appearance of samples	8	15	15	15
RDF C&I	RDF prepared from commercial & industrial waste (light weight fraction, PVC removal)	Particle size: < 50 mm slight differences between samples observable (e.g. different shares of aluminum compounds, plastic threads, paper scraps)	4	8	5	5
RDF MSW + C&I	RDF prepared from pre-processed municipal solid waste and commercial & industrial waste (light weight fraction)	Particle size: < 50 mm differences between samples observable (e.g. different shares and types of foamed plastics, fabrics, plastic threads)	4	8	5	6

RDF – refuse-derived fuel, C&I – commercial and industrial waste, MSW – municipal solid waste.
[1] Samples of 5–10 kg are drawn daily over a period of 7–15 days (see details in Supplementary material).

$$EF \text{ per unit mass in } kg_{CO_{2,fos}}/t_{RDF} = TC_{RDF,wf} * x_{F,TC} * M_{CO2}/M_C \quad (3)$$

$$EF \text{ per unit energy in } kg_{CO_{2,fos}}/GJ_{RDF} = (TC_{RDF,wf} * x_{F,TC} * M_{CO2}/M_C)/LHV_{RDF} \quad (4)$$

whereby LHV_{RDF} is the lower heating value of the RDF in GJ/t and M_{CO2} and M_C are the molar weights of CO_2 and carbon respectively in g/mol.

2.2. Samples and sample preparation

Three different types of solid RDFs are investigated in the study presented:
- Residues of a pulp and paper factory (**Paper Reject**)
- RDF prepared from commercial & industrial waste (**RDF C&I**)
- RDF prepared from pre-processed municipal solid waste and commercial & industrial waste (**RDF MSW + C&I**)

Details on the RDF types are provided in Table 2. Samples are drawn over a period of 15 days (Paper Reject) and 8 days (RDF C&I and RDF MSW + C&I). Each sample comprises 5–10 kg of dry matter (which corresponds to around 60 L). Samples of all three RDFs are analyzed by means of the ^{14}C-Method, aBM, SDM, and MS. Due to time and budget constraints, only the aBM could be applied to all drawn samples. The presented comparisons between methods are all based on the same respective samples (e.g. the same 8 Paper Reject samples are considered when ^{14}C-method is compared to aBM).

For the elemental analysis (necessary to determine the elemental composition of the RDF samples TOX_{RDF}) a final sample size of only a few centigrams is required (10–40 mg for single determination). Thus, an elaborate sample preparation procedure (comminution, reduction) is necessary to ensure reliable analytical results. The procedure of sample preparation applied within the study is shown in Fig. 2. It is carried out in agreement with EN 15413:2011 and based on findings in previous works of the authors [23].

Around 4 kg per sample are milled down to a grain size of < 4 mm by means of a cutting mill (Essa CM 1000). The sample < 4 mm is reduced to around 500 g using a riffle divider and further milled down to < 1 mm (by cutting mill Retsch SM 2000). After another splitting step using a riffle divider, one part of the 1 mm sample is set aside to apply the Selective Dissolution Method (Section 2.5.1). Another part (around 60 g) is further treated with an ultra-centrifugal mill (Retsch ZM 200) to receive a sample with a final grain size of < 0.5 mm. A rotary divider (Retsch, PT 100) is applied and, finally, 15 g are comminuted by a cryogenic mixer mill (Cryomill, Retsch) whose milling bin is cooled by liquid nitrogen. This final preparation step is done in order to facilitate the proper grinding of the cellulose fibers present in the sample. Despite the lack of a Cryomill sieve, a further grain size reduction (down to < 0.2 mm) can be expected by the last milling step (confirmed in [23]). The finely ground analysis sample is used for analyses necessary for the aBM and the ^{14}C-Method.

2.3. Determination of the elemental composition of biogenic and fossil organic matter present in RDF (Manual Sorting)

In order to examine the robustness and validity of input parameters of the adapted Balance Method, new input data on the elemental composition of the water-and-ash-free biogenic and fossil matter (TOX_{BIO} and TOX_{FOS}) are generated from the samples investigated. This is done by sorting samples of all three RDF types and analyzing the biogenic and fossil matter in the RDFs. The so generated data for the RDFs can then be compared with each other and to literature-derived values (e.g. [24]). This is to appraise the variability and universality of the aBM-input parameter (TOX_{BIO} and TOX_{FOS}).

Around 4 kg per RDF are sorted into 9 categories: *cardboard/paper*, *wood*, *plastic*, *textiles*, *organic*, *rubber*, *composite & impure materials*, *fine fraction < 2 cm*, *metals & inert*. In order to estimate TOX_{BIO} and TOX_{FOS} present in the RDF, a rough mass share of biogenic and fossil matter is appraised for each sorted compound. The organic parts in *cardboard/paper*, *wood*, and *organic* are generally regarded as biogenic, and *plastics* are expected to be produced from fossil sources. Yet, some "contaminations" are expected in these constituents due to e.g. partly-dissolved paper fibers attached to plastics or undetectable impregnated cardboard. For the other compounds, the appraisal on the biogenic and fossil share is even more challenging, particularly for *textiles* (mix of natural and synthetic fibers), *rubber* (mix of natural and synthetic rubber), *composite & impure materials* (mix of cardboard, different polymers, etc.), and the *fine fraction < 2 cm* (mix of generally all compounds mentioned).

Thus, the appraisal on the rough mass share of biogenic and fossil matter in the sorted compounds is carried out by
(1) a preliminary evaluation by means of the aBM, using analyses of the sorted compounds (*TOC*, *TOH*, *TOO*, *TON*, and *TOS* determined according to Eq. (3)) and literature data for TOX_{BIO} and TOX_{FOS} as input values,
(2) applying the Selective Dissolution Method (see Section 2.5.1) for selected compounds, and by
(3) conducting Radiocarbon analyses (see Section 2.5.2) for selected compounds

For (1), the following assumptions are made:
- Natural *textiles* are mainly composed of cellulose (90 wt%) and wool (10 wt%) (based on Kost, 2001 [34]).
- Synthetic *textiles* are composed of polyamide (30 wt%), polyester (49 wt%), polyacrylonitrile (15 wt%) and polypropylene (6 wt%) (based on Kost, 2001 [34]).
- Compounds of *rubber* and *organic* are negligible (shares of below 1 wt% are found in the RDFs by manual sorting).
- *Composite & impure materials* mainly contain cardboard and plastics, whereby the elemental composition of these compounds is assumed to correspond to the average elemental composition found for paper

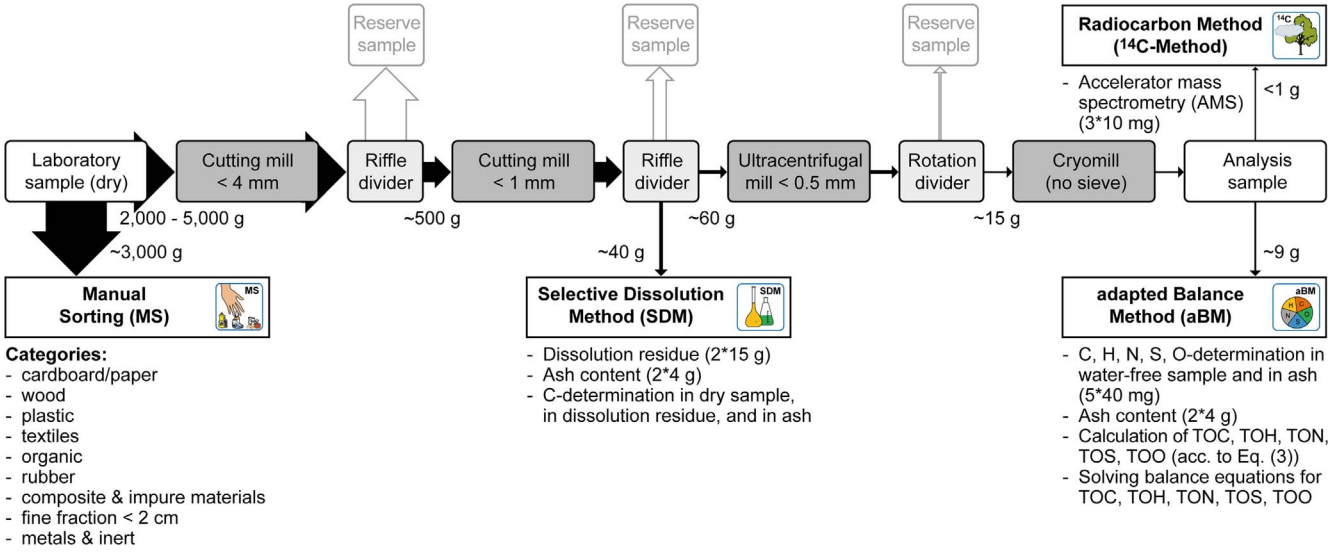

Fig. 2. Sample preparation procedure and analysis methods applied (it has to be noticed that the four analysis methods have not been applied to all RDF samples taken).

and mixed plastics in municipal solid waste in Kost (2001) [34] (values are provided in Supplementary material Table D.2).

- *Metals & inert* compounds are sorted at 100% sorting precision, thus they are not relevant for the investigations and are not further considered.

Additional sortings of the *fine fraction < 2 cm* are conducted in order to appraise the rough composition of this compound. In total around 400 g of the fine fraction of Paper Reject (from different samples) and around 140 g of RDF C&I and RDF MSW + C&I (from different samples) are sorted into the same categories as for the primary sorting. It is assumed that the average sorting results of the *fine fraction < 2 cm* apply to the fine fractions of all samples of the same RDF. An overall composition of the RDFs in terms of compounds is calculated, taking the results of the primary sorting and the fine fraction sorting into account (the sorting results are provided in the Supplementary material Table C.1).

Table 3 provides the biogenic mass share considered in each sorted compound. These shares are used together with values for *TOX* of each compound (*TOC*, *TOH*, *TOO*, *TON*, and *TOS*) to appraise typical ranges for TOX_{BIO} and TOX_{FOS} in the three RDF types. *TOX* values are used from own analyses results for *cardboard/paper*, *wood* and *plastic*; values for natural and synthetic textiles as well as for cardboard/paper and plastics in the composite compounds are based on Kost (2001) [34] (values in Supplementary material Table D.2). This procedure for deriving ranges for TOX_{BIO} and TOX_{FOS} is confirmed to be appropriate in Schwarzböck et al. (2017) [36].

The definition of TOX_{BIO} and TOX_{FOS} for each RDF is generally required for the application of aBM but needs to be determined only once for each type of RDF and can then be utilized for this type of RDF, unless major changes in the composition of biogenic and fossil organic matter are expected (e.g. change of waste collection scheme for certain plastics).

2.4. Chemical analyses

2.4.1. Water content and ash content

The water content of each laboratory sample is determined by drying the unprepared sample at 105 °C for at least 24 h (start of drying directly after the delivery to the laboratory). For each analysis sample the ash content is analyzed in duplicate and in accordance with EN 15403:2011 [37]. To this end, 4 g material of each sample are dried at 105 °C for 24 h before being combusted at 350 °C in a muffle furnace for one hour and at 550 °C for four hours under air injection. All weights of the sample (before drying, after drying, after ignition) are recorded (Sartorius Entris) in order to calculate the ash content.

2.4.2. Elemental analysis and determination of TOX_{RDF} (for the adapted Balance Method)

The water-free (dried at 105 °C for 24 h) analysis samples are analyzed for the elemental composition using an Elementar Vario Macro instrument (Elementar Analysensysteme GmbH, Langenselbold,

Table 3
Appraised biogenic share in the different sorted compounds of the RDFs.

	Compound	Biogenic share in wt%,wf			
		Paper Reject	RDF C&I	RDF MSW + C&I	acc. to EN 15440:2011[1]
1	*Cardboard/paper*	93	93	92	100
2	*Wood*	99	99	99	100
3	*Plastic*	5	4	8	0
4	*Textiles*	65	45	45	50
5	*Organic*	disregarded (< 1 wt%)	disregarded (< 1 wt%)	disregarded (< 1 wt%)	100
6	*Rubber*	disregarded (< 1 wt%)	disregarded (< 1 wt%)	disregarded (< 1 wt%)	80
7	*Composite and impure materials*	34	58	46	–
8	*Fine fraction < 2 cm*	60	45	38	50
9	*Metals & inert*	0	0	0	0

RDF – refuse-derived fuel, C&I – commercial and industrial waste, MSW – municipal solid waste, wt%,wf – weight percent on water-free basis.
[1] Information given in EN 15440:2011 on the biogenic shares is relevant for Manual Sorting (MS) only and is not considered for the adapted Balance Method (aBM).

Germany). At a combustion temperature of 1150 °C, the total carbon *TC*, total hydrogen *TH*, total nitrogen *TN*, and total sulfur *TS* content is determined according to DIN 51732:2014 [38]. Five measurements per sample are carried out, each of them comprising around 40 mg of sample material.

The total oxygen content *TO* is determined using an Elementar Vario EL instrument (Elementar Analysensysteme GmbH, Langenselbold, Germany). The analysis is based on the pyrolysis of the sample at 1150 °C and the conversion of all oxygen into carbon monoxide. For the analysis of *TO*, sample specimens of only 4 mg are used and 7 measurements per sample are conducted (due to limitations of the analyzer, allowing maximum 2 mg oxygen absolute).

Each analytical sequence is accompanied by verification samples and blanks to assure accuracy of the measurement result and to control disturbed baselines. Calibration correction factors are determined with set control limits of 5% (for C, N, S) or 10% (for H, O) (according to DIN 51732:2014 and manufacturer information; see also Supplementary material Table K.1 and Table K.2).

Each RDF-analysis sample is analyzed. In addition, the ignition residue of each test sample treated in the muffle oven is analyzed for its elemental composition to appraise the total inorganic content of carbon *TIC*, hydrogen *TIH*, nitrogen *TIN*, sulfur *TIS* and oxygen *TIO*. The values measured are converted according to Eq. (3) in order to determine the elemental composition on a water-and-ash-free reference basis.

$$TOX_{RDF} = (TX_{wf} - TIX_{wf} * A)/(1-A) \quad (5)$$

whereby TOX_{RDF} represents the total organic content of the respective element (*X…C, H, N, S, O*) in the water-and-ash-free sample in g/kg$_{waf}$, TX_{wf} the total content of the respective element in the water-free sample in g/kg$_{wf}$, TIX_{wf} the total inorganic content of the respective element in the water-free ash in g/kg$_{wf}$, and *A* the ash content on a water-free basis in kg/kg$_{wf}$. The values obtained thereby for total organic carbon *TOC*, total organic hydrogen *TOH*, total organic nitrogen *TON*, total organic sulfur *TOS*, and total organic oxygen *TOO* are summarized as TOX_{RDF}. They represent the input data required for the adapted Balance Method (additionally to TOX_{BIO}, TOX_{FOS}; see Section 2.3) (results for TOX_{RDF} are given in Supplementary material Table D.1).

2.5. Application of other methods (alternatively to adapted Balance Method)

In order to compare the results obtained by the aBM to results of standardized methods, the Selective Dissolution Method (SDM) and the Radiocarbon Method (^{14}C-Method) are applied according to Standard EN 15440:2011 [17]. Additionally, the sorting results can be used to derive the fossil mass fraction based on the Manual Sorting method (MS) (also described in EN 15440:2011).

2.5.1. Selective Dissolution Method (SDM)

The Selective Dissolution Method (SDM) relies on the assumption that biogenic components will selectively dissolve and oxidize when concentrated sulphuric acid and hydrogen peroxide are applied. The fossil components are expected to remain in the dissolution residue.

Various materials do not entirely act in accordance with this assumption of selective dissolution and can introduce errors to the results of the SDM [1,17,25,39]. For example, polymers originating from fossil fuel containing amino groups are almost entirely dissolved (up to 100%) when applying the SDM (e.g. nylon or polyurethane). For viscose and wool, both in large parts biomass, the biogenic content is reported to be underestimated by SDM up to 40%. Other polymers which originate from biomass but are re-engineered at molecular level (e.g. rubber) can be non-selectively dissolved in the range of 15–100% [1]. Thus, when high (unknown) shares of materials are present which do not react according to the assumptions of the SDM, the reliability of the results of the SDM is rather limited.

For the investigations presented, the SDM is applied as described in EN 15440:2011. Threefold test portions are used (15 g; double determination) in order to account for the rather heterogeneous samples (particles sizes of <1 mm are used as stipulated in EN 15440:2011). The carbon content is determined in the <1 mm sample, in the dissolution residue, and in the ignition residue using an Elementar Vario Macro instrument (Elementar Analysensysteme GmbH, Langenselbold, Germany). Equations are provided in EN 15440:2011 and in Supplementary material B.

In total, 25 samples are analyzed according to the SDM (15 Paper Reject-, 5 RDF C&I-, 5 RDF MSW + C&I-samples).

The uncertainty of the results is estimated from the duplicate determination (repeatability) and from values for the reproducibility of the method given in Table F.1.4 in EN 15440:2011.

2.5.2. Radiocarbon Method (^{14}C-Method)

The Radiocarbon Method (^{14}C-Method) is based on different ratios of carbon isotopes ^{14}C and ^{12}C in biogenic and fossil materials. F^{14}C is defined as ^{14}C/^{12}C ratio of a sample related to the level of this isotopic ratio for the reference year 1950 [40]. Consequently, biogenic materials show a value of ~1, whereas ^{14}C is extinct in fossil materials corresponding to an F^{14}C value of 0. In order to determine the fraction of biogenic carbon, it is necessary to know the F^{14}C values in the sample and in pure biogenic materials present in the waste (i.e. the F^{14}C reference value). The latter depends on the type of biomass and on the period of growth, and dominates the uncertainty of the method. This is due to the changing radiocarbon content in the atmosphere in the past century caused by nuclear weapon tests [28,29,39,41]. However, the ^{14}C-Method is regarded as a reliable method for the determination of the biomass content in secondary fuels as it has the lowest analytical uncertainty (accelerator mass spectrometry AMS < 3–7% relative [29,42–44]). Liquid Scintillation Counting (LSC) can also be applied to analyze the ^{14}C content [25,41].

Within the study presented, radiocarbon analyses according to EN 15440:2011 using AMS are conducted ([45]) for the finely ground analysis samples (see Section 2.2). A triplicate determination with each 10 mg is chosen. In total, 16 samples are analyzed (8 Paper Reject-, 4 RDF C&I-, 4 RDF MSW + C&I-samples). F^{14}C reference values applied within the study are provided in Table 5. F^{14}C reference values for the ^{14}C content of pure biogenic matter in RDF C&I and RDF MSW + C&I are estimated according to Mohn et al. (2008) [29] (see Table 4). Approximate shares of cardboard, wood, textiles, and fresh biomass (<0.5 wt%) in the biogenic fraction are used from sorting results and their respective biogenic shares (given in Table 3) are considered. ^{14}C analyses of pure cardboard/paper sorted out of the Paper Reject samples are used to derive the F^{14}C reference value for this RDF type. Thereby, the uncertainty of the F^{14}C reference value for ^{14}C-Method could be reduced as the cardboard/paper represents the major constituent in the biogenic matter of Paper Reject (around 92 wt%). A F^{14}C

Table 4
^{14}C content (given as mean and standard uncertainty) of biomass compounds used as reference value within the study ([29], value for Cardboard/paper in Paper Reject analytically determined).

^{14}C content F^{14}C$_{bio}$ [pMC]	Cardboard/paper	Wood	Textiles	Fresh biomass
Paper Reject	1.076 ± 0.020	1.150 ± 0.098	1.058 ± 0.036	1.015 ± 0.015
RDF C&I, RDF MSW + C&I	1.101 ± 0.024	1.150 ± 0.098	1.058 ± 0.036	1.015 ± 0.015

Table 5
^{14}C content (given as mean and standard uncertainty) of biomass in RDFs used as reference value within the study (calculated according to [29] and based on own analyses for Paper Reject).

	Paper Reject	RDF C&I	RDF MSW + C&I
^{14}C content $F^{14}C_{bio}$ [pMC]	1.080 ± 0.024	1.101 ± 0.038	1.088 ± 0.038

reference value of 1.080 ± 0.024 is determined for Paper Reject, indicating that the wood used for the cardboard/paper in this RDF has grown in more recent years than calculations by Mohn et al. (2008) [28] and Fellner et al. (2009) [29] would suggest. Equations to calculate the share of fossil carbon ($x_{F,TC}$) are provided in Mohn et al. (2008), in EN 15440:2011 and in Supplementary material B.

The uncertainty of the radiocarbon analysis results mainly from the ^{14}C reference value chosen (estimated as 3%rel). The heterogeneity of the rather small test specimens of only 10 mg accounts for 2–3%rel uncertainty (determined by triplicate determination).

Analyses by means of ^{14}C-Method reveal information on the fossil or biogenic carbon found in the RDF ($x_{F,TC}$, $x_{B,TC}$), while no information on the biogenic or fossil mass fraction ($x_{F,wf}$, $x_{B,wf}$) is ascertainable with this method. In order to still be able to compare the mass-related parameter to results of other methods as well, a conversion factor (derived from aBM results) is used within this study. An uncertainty of the conversion factor of 3%rel is considered.

2.5.3. Manual sorting (MS)

The samples are sorted into 9 categories (same sorting as described in Section 2.3): *cardboard/paper*, *wood*, *plastic*, *textiles*, *organic*, *rubber*, *composite & impure materials*, *fine fraction < 2 cm*, *metals & inert*. The *fine fraction < 2 cm* is represented by 24 wt% (RDF MSW + C&I) to 65 wt% (Paper Reject) of the total mass.

A biogenic share is assigned to each sorted compound according to EN 15440:2011 (values given in Table 3). The fossil mass fraction in the RDF can thereby be estimated. For the appraisal of the fossil carbon share in the samples, the carbon content of the fossil and biogenic matter in each compound is required. Within this study, values published in Kost (2001) [34] are used together with theoretical considerations (e.g. chemical structure of cellulose, polyethylene).

Due to the usually small or compressed constituent particles in RDF, a visual recognition is challenging and manual sorting is only attainable with great effort. At the same time, the uncertainty can hardly be quantified; also due to the strong dependence on a person's subjective categorization of particles. Within the study, the uncertainty of the manual sorting is estimated based on evaluations by aBM, by SDM, and ^{14}C-Method applied to selected sorted compounds (see Table 3 and Supplementary material B).

2.6. Statistical tests

Statistical tests are carried out in order to evaluate differences between data sets regarding their central tendencies (means) and variances. All tests are carried out using the program R (Version 3.0.2) [46] or DataLab (Version 3.530) [47]. In particular, the following tests are applied:

- Shapiro test: Test for normal distribution (required to decide which subsequent statistical test, e.g. t-Test, Wilcoxon rank sum test, is to be applied)
- 2-sample F-test: Test for homogeneity of variances between data sets; applied when there is no evidence that the data sets are not normally distributed
- Levene test: Test for homogeneity of variances between data sets; applied when there is evidence that the data sets are not normally distributed
- Paired *t*-test: Test for differences in means; applied when there is no indication that the differences between the data sets are not normally distributed
- Wilcoxon rank sum test (non-parametric test): Test for differences in means; applied when there is evidence that the differences between the data sets are not normally distributed

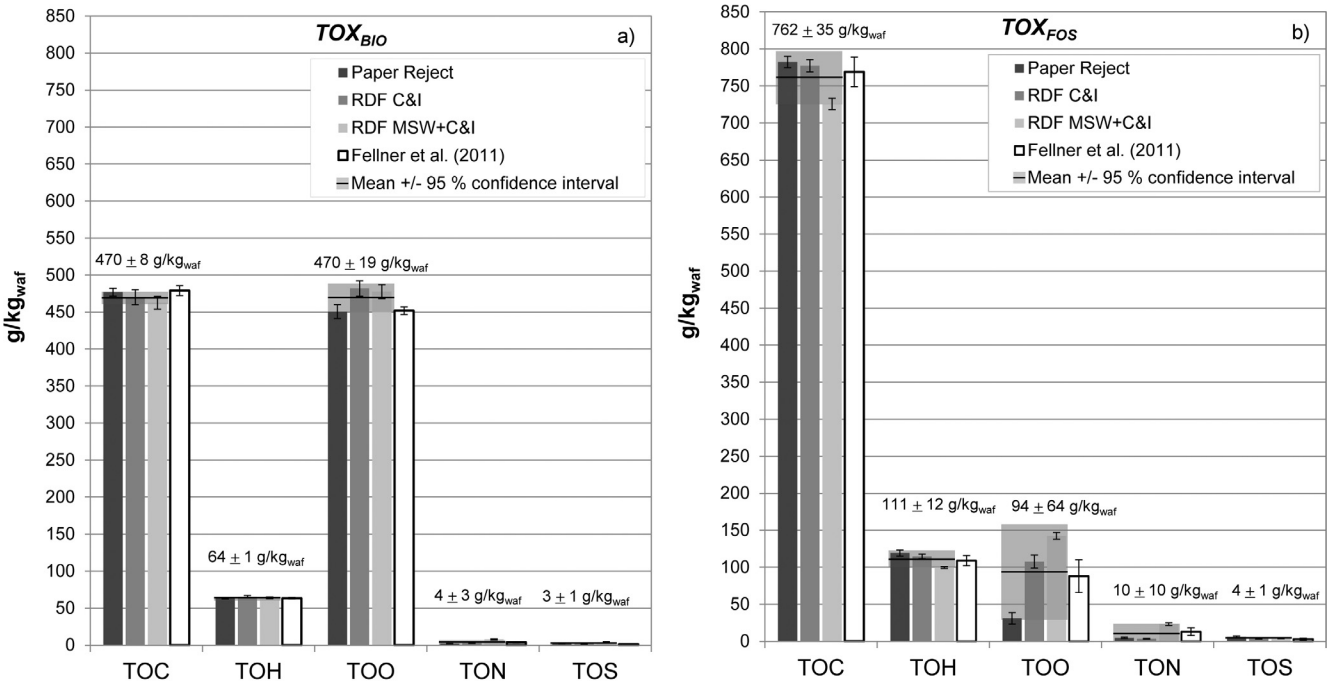

Fig. 3. Elemental composition of water-and-ash-free biogenic and fossil organic matter (TOX_{BIO}, TOX_{FOS}) present in RDFs investigated and compared to generic values given in Fellner et al. (2011) [24]. Values given indicate the means and 95% confidence intervals, taking data sets of the RDFs investigated into account.

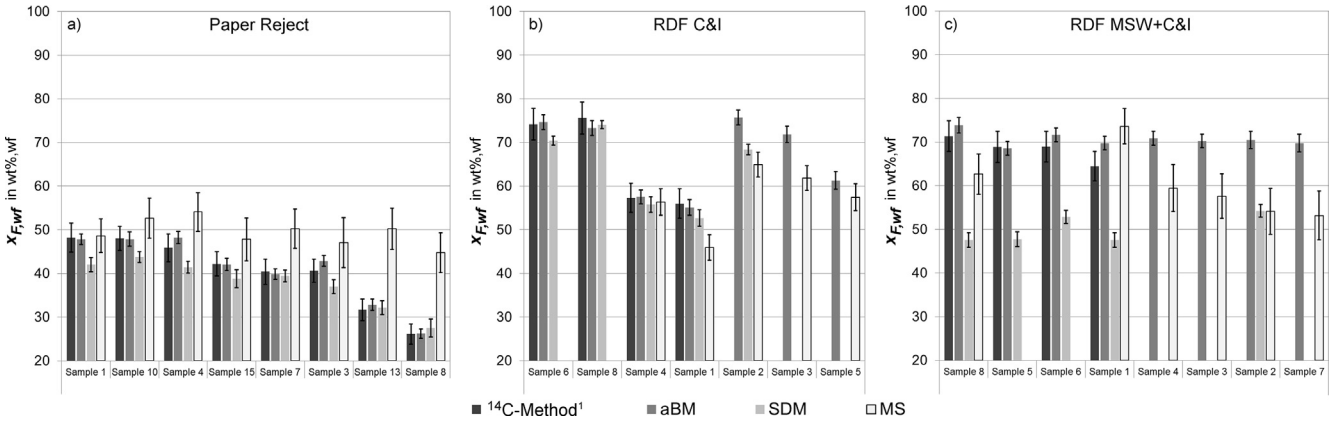

Fig. 4. Fossil mass fraction on water-free basis $x_{F,wf}$ determined for three RDF types by means of four different methods; error bars represent ± one standard deviation (note: not all samples could be analyzed by all methods due to time and budget constraints, see Table 2).
[1]^{14}C-Method: $x_{F,wf}$ is estimated based on $x_{F,TC}$ using a conversion factor determined by aBM results.

For all statistical tests a level of significance of 0.05 is used.

3. Results and discussion

3.1. Elemental composition of biogenic and fossil organic matter (TOX_{BIO}, TOX_{FOS})

The aBM requires data on TOX_{RDF} and on TOX_{BIO} and TOX_{FOS} present in the RDF sample. Within this study, TOX_{BIO}, TOX_{FOS} are determined by manual sorting and elemental analyses for each RDF type (see Section 2.3). Fig. 3 shows that the results obtained for the different RDFs are in a close range. They are similar to values given in Fellner et al. (2011) [24], where typical values for RDF processed from household and commercial waste are collected. *TOC* and *TOH* show a small variability with coefficient of variation <10%rel (in fossil organic matter) and <2%rel (in biogenic organic matter). The deviation from the literature values is below 2%rel for *TOC* and *TOH*. The most variable value is the *TOO* in the fossil organic matter, which varies by around 60%rel (deviation from literature values of 7%rel). This indicates a high dependence of the *TOO* content on the present polymer type in the RDF. A higher *TOO* content found in the fossil organic matter of RDF MSW + C&I signals higher shares of polyamide, polyethylene terephthalate, or polyurethane. In contrast, the Paper Reject can be estimated to contain high shares of polyethylene and polypropylene, which are characterized by a low or even zero oxygen content (and higher carbon and hydrogen content) compared to other polymers.

The composition of the biogenic matter tends to less variability compared to the composition of the fossil matter. The values derived for *TOC*, *TOH*, and *TOO* vary only by up to 4%rel (coefficient of variation) and deviate from the literature values below 4%rel. This confirms findings in Schwarzböck et al. (2017) [48] that the elemental composition of water-and-ash-free biogenic matter in wastes is almost independent of the shares of the different biogenic compounds (e.g. wood, paper, food waste, textiles). A probable range for the elemental composition of water-and-ash-free biogenic organic matter can thus be easily derived, also without extensive sorting analyses. Recent investigations even indicate that there are typical values for TOX_{BIO} and TOX_{FOS} depending on the RDF type [36]. Thus, the initial workload for sorting analyses could be saved at all, once there is a database available.

3.2. Fossil mass fraction and share of fossil carbon in the RDF samples determined by different methods

3.2.1. Comparison in terms of variance and differences between methods

The fossil mass fraction ($x_{F,wf}$) and the share of fossil carbon ($x_{F,TC}$) in the RDF samples is calculated by means of aBM and three standardized methods as described in Sections 2.1 and 2.5. Generally, the carbon-related figure ($x_{F,TC}$) – unlike the mass-related parameter ($x_{F,wf}$) – is less dependent on the ash content in the RDF and is directly related to the heating value. As visible from Fig. 6 to Fig. 8, $x_{F,TC}$ is at least 6% abs higher than $x_{F,wf}$ due to the higher carbon content in fossil matter compared to biogenic matter. Assuming that all carbon (*TC*) in the RDF is oxidized to carbon dioxide (CO_2) during the combustion, $x_{F,TC}$ also

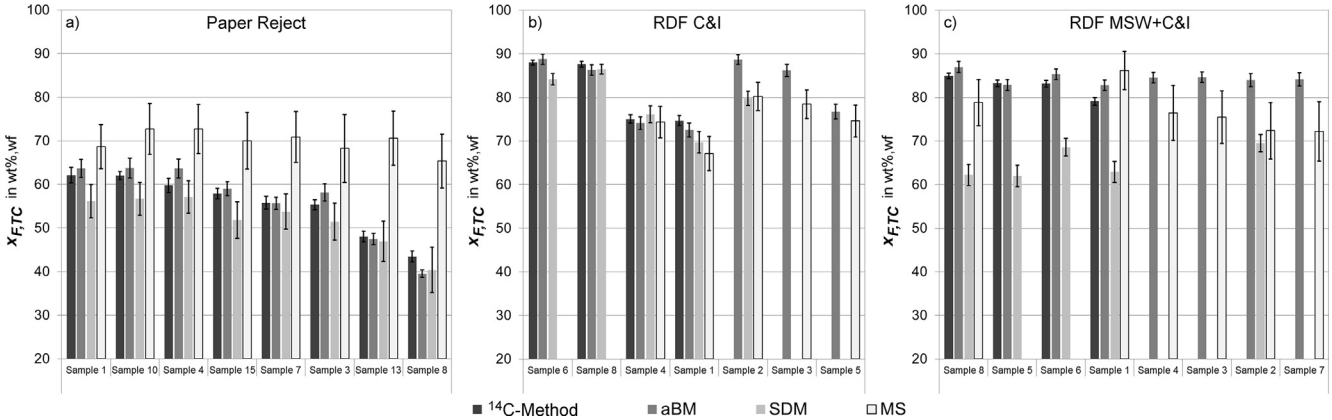

Fig. 5. Share of fossil carbon $x_{F,TC}$ determined for three RDF types by means of four different methods; error bars represent ± one standard deviation (note: not all samples could be analyzed by all methods due to time and budget constraints, see Table 2).

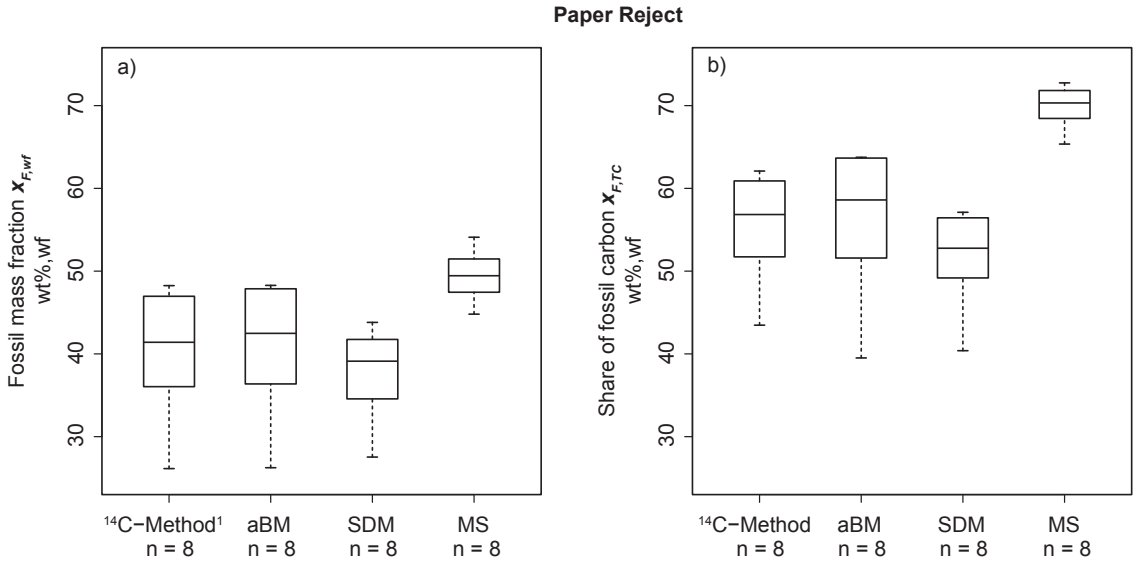

Fig. 6. Fossil mass fraction ($x_{F,wf}$) and share of fossil carbon ($x_{F,TC}$) in Paper Reject determined by four different methods.
[1] ^{14}C-Method: $x_{F,wf}$ is estimated based on $x_{F,TC}$ using a conversion factor determined by aBM results.

represents the share of fossil CO_2 related to the total CO_2 emitted during incineration.

Paper Reject (Fig. 4a), Fig. 5a), and Fig. 6):
In the Paper Reject samples, the aBM reveals fractions of fossil matter $x_{F,wf}$ (represented mainly by plastics) between 26 and 48 wt % and shares of fossil carbon $x_{F,TC}$ between 39 and 64 wt%. An average ash content of 7 wt% in the Paper Reject results in $x_{F,TC}$ being 12 to 18%abs above $x_{F,wf}$ (Fig. 4 and Fig. 5).
The aBM delivers results in a similar range as the ^{14}C-Method ($x_{F,wf}$ 26–48 wt% and $x_{F,TC}$ 43–62 wt%). The **variance** between the samples for the aBM and ^{14}C-Method cannot be observed to be significantly different (based on a 2-sample F-test). Standard deviations of 8.7%abs are found for $x_{F,TC}$-values generated by aBM and 6.7% abs for values of ^{14}C-Method, indicating a similar dispersion of the method's results (visible from Fig. 6).
Fig. 6 shows that the results for SDM applied to Paper Reject are in a slightly smaller range than for the ^{14}C-Method and aBM (standard deviation of 5.7%abs for SDM). A significant difference in variance of the SDM-sample results compared to ^{14}C-Method and aBM can, however, not be observed (based on 2-sample F-tests). Different findings for Paper Reject samples evaluated based on MS: Significantly smaller dispersion is found (standard deviation $x_{F,TC}$ of 2.5%abs) compared to ^{14}C-Method-, aBM-, and SDM-results. It is assumed that differences in the composition of the samples are barely detectable by MS.
Comparing the mean values obtained – $x_{F,wf}$ and $x_{F,TC}$ – by aBM and ^{14}C-Method for Paper Reject, no significant **differences** are found between the two methods (based on statistical tests, indicated in Table 6 by significance codes). The deviations in results of the aBM and the ^{14}C-Method are in the range of −3.9 to +4.0 wt%abs ($x_{F,TC}$). Mean deviations of +0.6 wt%abs for $x_{F,wf}$ and +0.8 wt% abs for $x_{F,TC}$ are found (Table 6). The ranges of uncertainty of the two approaches overlap each other for all 8 samples compared, with the exception of two samples when $x_{F,TC}$ is regarded (Sample 4 and Sample 8 in Fig. 5a)).
Based on statistical tests, the results of SDM compared to aBM and ^{14}C-Method differ significantly. With a deviation between −6.1 wt %abs and −1.2 wt%abs ($x_{F,TC}$) from ^{14}C-Method, the SDM appears to underrate the fossil share in the Paper Reject by trend. The ranges of uncertainty between SDM and ^{14}C-Method overlap for 5 of 8 samples (Fig. 5a)). This could be explained by the fact that glue residues which are found in the samples might represent soluble polymers (e.g. based on amino groups) and are misleadingly declared biogenic by the SDM (but actually are of fossil origin). A mean deviation of −2.6 wt%abs ($x_{F,wf}$) and −3.8 wt%abs ($x_{F,TC}$), however, can be regarded as in rather good agreement with the ^{14}C-Method when the uncertainties of the methods and results found in other studies are taken into consideration [31,33]. For example, Muir et al. (2015) [25] reported 30–35 wt%abs underestimation by

Table 6
Results for Paper Reject: Fossil mass fraction ($x_{F,wf}$) and share of fossil carbon ($x_{F,TC}$); means of different methods and deviations from results of ^{14}C-Method.

Method	Fossil mass fraction $x_{F,wf}$			Share of fossil carbon $x_{F,TC}$		
	Mean ± SD wt%,wf	Dev.^{14}C wt%abs,wf	Sign.	Mean ± SD wt%,wf	Dev.^{14}C wt%abs,wf	Sign.
^{14}C-Method	40.4 ± 1.0[1]	–		55.6 ± 0.5	–	
aBM	41.0 ± 0.5	+0.6	(–)	56.4 ± 0.7	+0.8	(–)
SDM	37.8 ± 0.6	−2.6	(*)	51.8 ± 1.5	−3.8	(***)
MS	49.5 ± 1.3	+9.1	(***)	69.9 ± 1.6	+14.3	(***)

Significance codes: (–) p > .1; ( ) p < .1; (*) .05 ≥ p > .01; (**) .01 ≥ p > .001; (***) .001 ≥ p with (***) indicating the highest significance.
SD – Standard deviation, representing the analytical uncertainty (derived per method as described in Section 2.5 and considering the number of samples n given in Fig. 6), wt%,wf – weight percent on water-free basis, Dev.^{14}C – Mean deviation from result of ^{14}C-Method as absolute percentage (negative = result is lower than result of ^{14}C-Method), Sign. – Significance level for Dev.^{14}C.
[1] ^{14}C-Method: $x_{F,wf}$ is estimated based on $x_{F,TC}$ using a conversion factor determined by aBM results.

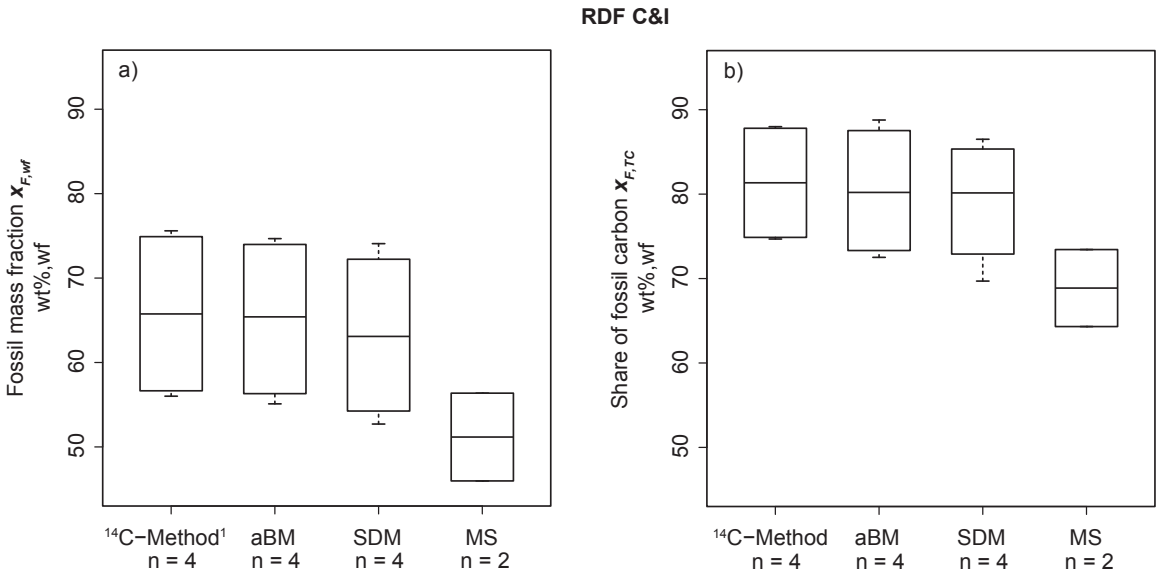

Fig. 7. Fossil mass fraction ($x_{F,wf}$) and share of fossil carbon ($x_{F,TC}$) in RDF C&I determined by four different methods.
[1]^{14}C-Method: $x_{F,wf}$ is estimated based on $x_{F,TC}$ using a conversion factor determined by aBM results.

SDM compared to ^{14}C-Method when investigating the fossil energy share in MSW samples.

MS appears to significantly overestimate the fossil mass fraction $x_{F,wf}$ in the Paper Reject samples. Results of 0.4–19 wt%abs above ^{14}C-Method (mean deviation of +9.1 wt%abs) are found. The uncertainty ranges overlap each other for 4 of 8 samples (Fig. 4a)). Even higher differences between the MS results and the other methods can be observed when $x_{F,TC}$ is considered (Fig. 5a)). A mean deviation of +14.3 wt%abs compared to ^{14}C-results (and aBM results) is detected (see Table 6). A statistical test confirms a significant difference between the MS and ^{14}C-Method for Paper Reject samples (paired 2 sample *t*-test; significance indicated by codes in Table 6). This overestimation of the fossil fraction by MS can be ascribed to the following three factors: (1) The sorting category *fine fraction < 2 cm* is found to represent almost 65 wt% in the Paper Reject samples. According to EN 15440:2011, the fossil share in this category can be estimated to be 50 wt%. Based on further sorting and analyses (see Section 2.3), however, only 40 wt% of the *fine fraction < 2 cm* is estimated to actually be of fossil origin. This implies an approximately 5–6%abs systematic overestimation when adhering to the assumptions in EN 15440:2011. (2) The fact that the mass-based parameter ($x_{F,wf}$) is in better agreement with the other methods than the carbon-based figure ($x_{F,TC}$) indicates that inaccuracies are introduced by the utilization of literature values to derive the fossil carbon content from the manual sorting results (Supplementary material B). The carbon content considered in biogenic matter (TOC_{BIO}) as estimated from literature values is found to be almost 9%abs (90 $gC_{bio}/kg_{waf,bio}$) lower (allegedly underestimated) than the TOC_{BIO} determined by analyses. Together with the inaccuracy from (1), this coincides with the mean deviation of MS results from ^{14}C-Method results (+14 wt%abs). (3) Partly-dissolved cardboard pieces and cellulose fibers attached to plastics lead to difficulties in manually separating these materials. This factor presumably contributed to an overestimation of the plastics compound during sorting. Only extensive additional investigations can provide estimates on this error. Appraisals within this study reveal that the sorted plastics compound contains around 5 wt% of biogenic particles (Table 3).

It can be estimated from the aBM results that the fossil mass fraction in the reject of the paper and board factory considered is around 38%wt (on a dry basis) and can vary ±7 wt%abs. The share of fossil carbon is expected to be 54 wt% with a variability of ±8 wt%abs (standard deviation between sample results). Thus, around 54 wt% of the CO_2 emissions originating from the combustion of the Paper Reject would need to be counted as climate-relevant. These results are derived from aBM analyses of all 15 Paper Reject samples (only 8 are shown in Fig. 4a) and Fig. 5a) as for the other 7 no other method than aBM is applied; results of all samples are provided in the Supplementary material Table H.1).

RDF C&I (Fig. 4b), Fig. 5b), and Fig. 7):

When RDF C&I samples are considered, ^{14}C-Method, aBM and SDM all show a similar dispersion of the sample results (Fig. 7). A standard deviation between the samples of around 10 wt%abs for $x_{F,wf}$ and around 8 wt%abs for $x_{F,TC}$ is found (based on same 4 samples, shown in Fig. 4b) and Fig. 5b)). No significant differences in variance between the four methods can be found.

Low deviations between results of different methods for $x_{F,wf}$ and for $x_{F,TC}$ are found when RDF C&I samples are regarded. The differences in means between the methods are not found to be significant based on statistical tests. Comparing aBM with ^{14}C-Method, the mean deviation of the share of fossil carbon $x_{F,TC}$ is −0.9 wt%abs, which can be counted as good agreement between these methods (Table 7). As seen from Fig. 4b) and Fig. 5b), the range of uncertainty overlaps for all RDF C&I samples when aBM and ^{14}C-Method are considered.

Slight underestimations by SDM of $x_{F,wf}$ and $x_{F,TC}$ are observed when comparing the figures to ^{14}C-Method results (mean deviation −2.6 wt%abs for $x_{F,wf}$ and −2.2 wt%abs for $x_{F,TC}$ – Table 7). However, statistical tests do only indicate a fairly significant difference for $x_{F,wf}$ and the ranges of uncertainty overlap for all 4 samples ($x_{F,wf}$). This is regarded as rather good agreement.

As there are only 2 MS values available for RDF C&I to be compared to the ^{14}C-Method, no clear statement on an over-underestimation can be provided. Contrary to the findings for Paper Reject, the carbon content considered in the biogenic matter and fossil matter (TOC_{BIO}, TOC_{FOS}) which is necessary to derive $x_{F,TC}$ from $x_{F,wf}$ does affect the observed difference to ^{14}C-Method results only marginally (deviation from ^{14}C-Method of around −6 wt%abs for both parameters).

When all 8 samples of RDF C&I are considered (Fig. 4b) and Fig. 5b)), the aBM delivers fossil mass fractions of 55–76 wt% with a standard deviation of 8 wt%abs between the samples. Thus, it can be expected that the composition of this RDF can vary considerably with time and

Table 7
Results for RDF C&I: Fossil mass fraction ($x_{F,wf}$) and share of fossil carbon ($x_{F,TC}$); means of different methods and deviations from results of ^{14}C-Method.

Method	Fossil mass fraction $x_{F,wf}$			Share of fossil carbon $x_{F,TC}$		
	Mean ± SD wt%,wf	Dev.^{14}C wt%abs,wf	Sign.	Mean ± SD wt%,wf	Dev.^{14}C wt%abs,wf	Sign.
^{14}C-Method	65.8 ± 1.8[2]	–		81.3 ± 0.4	–	
aBM	65.2 ± 1.1	−0.6	(–)	80.4 ± 0.8	−0.9	(–)
SDM	63.2 ± 0.7	−2.6	(*)	79.1 ± 0.8	−2.2	(–)
MS[1]	51.2 ± 3.6	−5.5	(n.a.)	68.9 ± 2.6	−6.0	(n.a.)

Significance codes: (–) p > .1; ( ) p < .1; (*) .05 ≥ p > .01; (**) .01 ≥ p > .001; (***) .001 ≥ p with (***) indicating the highest significance.
SD – Standard deviation, representing the analytical uncertainty (derived per method as described in Section 2.5 and considering the number of samples n given in Fig. 7), wt%,wf – weight percent on water-free basis, Dev.^{14}C – Mean deviation from result of ^{14}C-Method as absolute percentage (negative = result is lower than result of ^{14}C-Method), Sign. – Significance level for Dev.^{14}C.
[1] MS: Dev.^{14}C refers to another ^{14}C-Method-mean value than presented here (as only two MS samples can be compared).
[2] ^{14}C-Method: $x_{F,wf}$ is estimated based on $x_{F,TC}$ using a conversion factor determined by aBM results.

representative analyses results require high experimental control (e.g. concerning samples sizes).

RDF MSW + C&I (Fig. 4c), Fig. 5c), and Fig. 8):

The different methods deliver a broad range of results for samples of RDF MSW + C&I (sample results presented in Fig. 4c) and Fig. 5c)). As already observed for Paper Reject and RDF C&I, there is good agreement between the results of aBM and ^{14}C-Method for RDF MSW + C&I samples (uncertainty ranges overlap for 3 of 4 samples; Fig. 4c) and Fig. 5c)). A mean deviation of $x_{F,wf}$ between aBM and ^{14}C-Method of +2.6 wt%abs is determined. Regarding $x_{F,TC}$, the deviation between these two methods is on average +1.9 wt%abs. The deviation is slightly higher compared to results of the other RDFs but no significant differences are found between aBM and ^{14}C-Method (Table 8).

Different observations are made when results of SDM are compared to ^{14}C-Method and aBM. As also observed for Paper Reject, the SDM constitutes a significantly lower $x_{F,wf}$ and $x_{F,TC}$. With a mean difference of −19.5 wt%abs for $x_{F,wf}$ and −18.7 wt%abs for $x_{F,TC}$, the deviation from ^{14}C-Method is even more distinctive for the RDF MSW + C&I samples than for the Paper Reject samples. It can be assumed that the RDF MSW + C&I samples contain significant shares of fossil materials which are dissolved when sulphuric acid is applied. For example, foamed plastics which are used in mattresses, furniture, building insulation, the automobile industry, etc., could be detected visually in all of the RDF MSW + C&I samples. These polymers, such as polyurethane, usually contain amino groups and are easily dissolved (almost entirely according to Cuperus et al., 2005 [1]). Additionally, an average share of 23 wt% of textiles is found in the RDF MSW + C&I samples. Textiles are expected to contain dissolvable fossil polymers (such as polyamide or nylon) and therefore introduce systematic errors into the results of the SDM.

For the 2 RDF MSW + C&I samples, where MS results can be compared to ^{14}C-Method results, very good agreement between MS and ^{14}C-Method is found. Yet, the very limited sample size makes is difficult to make out a clear trend.

3.2.2. Correlation of aBM results with results of standardized methods

In order to evaluate the agreement of the aBM results with the results of the standardized methods, a simple linear regression is performed. Fig. 9 shows the correlation curves for the share of fossil carbon ($x_{F,TC}$), divided according the method applied. The linear regression confirms that the values obtained by the aBM are in excellent agreement with the values of the **^{14}C-Method**. A correlation coefficient R^2 of 0.98 is found when all investigated samples are regarded as one dataset. A separate consideration of the RDFs (presented in the Supplementary material Fig. I.1) reveals that there is a strong relationship of aBM

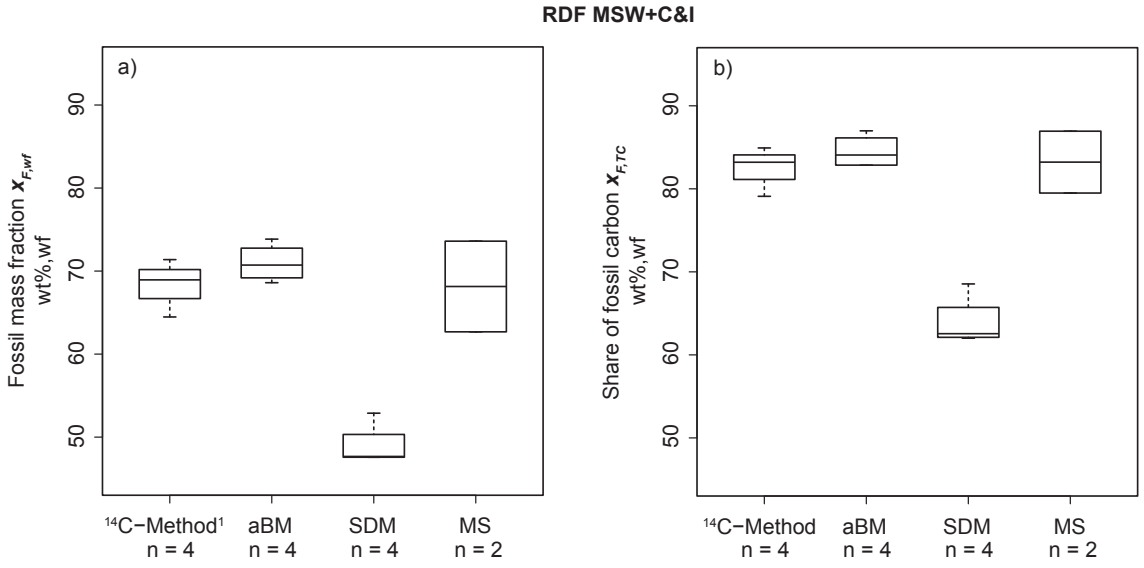

Fig. 8. Fossil mass fraction ($x_{F,wf}$) and share of fossil carbon ($x_{F,TC}$) in RDF MSW + C&I determined by four different methods.
[1]^{14}C-Method: $x_{F,wf}$ is estimated based on $x_{F,TC}$ using a conversion factor determined by aBM results.

Table 8
Results for RDF MSW + C&I: Fossil mass fraction ($x_{F,wf}$) and share of fossil carbon ($x_{F,TC}$); means of different methods and deviations from results of ^{14}C-Method.

Method	Fossil mass fraction $x_{F,wf}$			Share of fossil carbon $x_{F,TC}$		
	Mean ± SD wt%,wf	Dev.^{14}C wt%abs,wf	Sign.	Mean ± SD wt%,wf	Dev.^{14}C wt%abs,wf	Sign.
^{14}C-Method	68.4 ± 1.7	–		82.6 ± 0.4	–	
aBM	71.0 ± 1.4	+2.6	(–)	84.5 ± 1.0	+1.9	(–)
SDM	48.9 ± 0.8	−19.5	(**)	63.9 ± 1.2	−18.7	(**)
MS[1]	68.1 ± 3.4	−0.2	(n.a.)	83.2 ± 3.9	+1.2	(n.a.)

Significance codes: (–) p > .1; ( ) p < .1; (*) .05 ≥ p > .01; (**) .01 ≥ p > .001; (***) .001 ≥ p with (***) indicating the highest significance.
SD – Standard deviation, representing the analytical uncertainty (derived per method as described in Section 2.5 and considering the number of samples n given in Fig. 8), wt%,wf – weight percent on water-free basis, Dev.^{14}C – Mean deviation from result of ^{14}C-Method as absolute percentage (negative = result is lower than result of ^{14}C-Method), Sign. – Significance level for Dev.^{14}C.
[1] MS: Dev.^{14}C refers to another ^{14}C-Method-mean value than presented here (as only two MS samples can be compared).

results with ^{14}C-Method values for Paper Reject and for RDF C&I. The correlation for RDF MSW + C&I-samples is found to be moderate, with a correlation coefficient of 0.53. The linear regression line is, however, for this RDF also close to the ideal correlation with a low intercept (6.93) and a slope of almost 1 (0.90).

The **SDM** results for all investigated samples in Fig. 9 can be regarded as in relatively good agreement with the aBM figures, with a correlation coefficient R^2 of 0.79. Yet, it can already be seen that the regression line is skewed by RDF MSW + C&I samples in the upper range of the graph. This leads to an overall slope of 0.69, which is clearly below the ideal correlation (1). For RDF MSW + C&I there is no detectable linear relationship of aBM results with SDM results ($R^2 < 0.1$). The regression line of aBM versus MS is rather weak, with a high absolute intercept and a slope different from 1 despite the moderate correlation coefficient of 0.64 (graph shown in Supplementary material Fig. I.1). Thus, for RDF MSW + C&I a reliable determination of the fossil content by means of the available methods appears the most challenging. It is expected that especially the composition of the fossil fraction (plastics and synthetic fibers) is the most decisive factor for the inaccuracies of the determination methods. The fact that there is no clear correlation between results of aBM and SDM indicates that the error due to non-selective dissolution of certain materials by SDM is not consistent with the samples considered. This implies that the content of dissolvable fossil polymers (foamed plastics, synthetic fibers) differs from one sample to the other.

SDM results can be considered to have a clear relationship to aBM results for the other RDFs (Paper Reject and RDF C&I). Correlation coefficients of 0.80 (Paper Reject) and 0.72 (RDF C&I) are determined (see Supplementary material Fig. I.1). However, in all cases, the slope deviates from the ideal correlation more than for ^{14}C-Method results. Thus, the relationship between the results of aBM and ^{14}C-Method is stronger than the one observed between the results of aBM and SDM.

A significant deviation from aBM is also noticeable when **MS** results are considered. A correlation coefficient of 0.52 is found when all RDFs are considered. The lowest correlation is found for Paper Reject with R^2 being only 0.22. The correlation between MS and aBM can only be considered as acceptable for one RDF (RDF C&I). A correlation coefficient of 0.78 indicates a good relationship for this RDF; the regression curve is found with a slope 0.74 (ideal = 1) and an intercept of 15.46 (ideal = 0). The regression line for RDF C&I is within a narrow range when ^{14}C-Method, SDM and MS are compared to aBM, meaning similar results are found with all methods. Yet, the relationship between ^{14}C-Method results and aBM is the most obvious (R^2 = 0.99, low intercept, slope almost 1). For Paper Reject and RDF MSW + C&I the linear

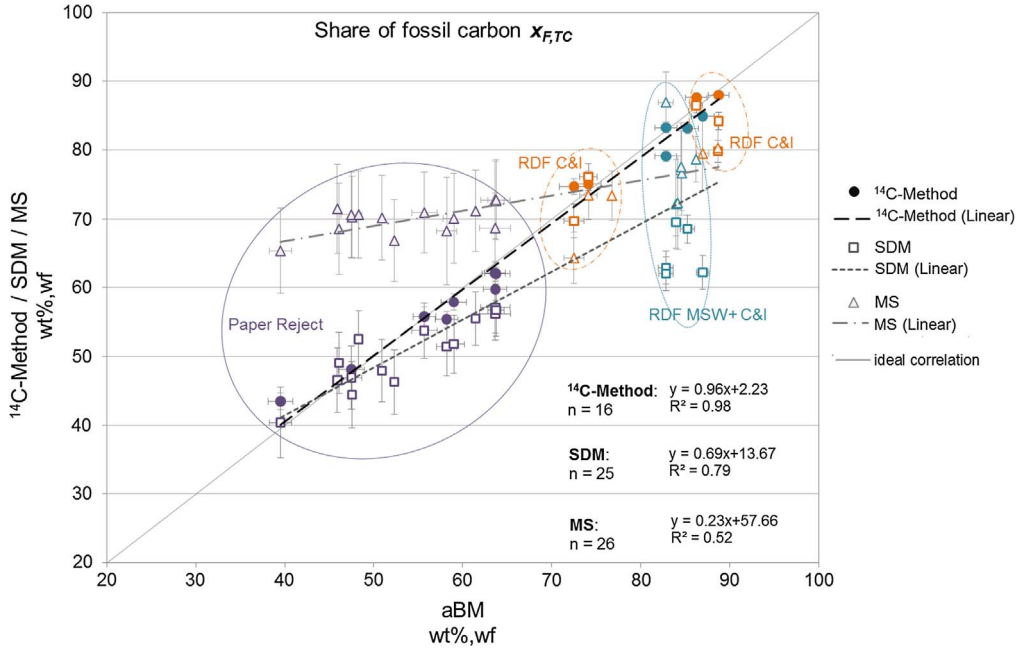

Fig. 9. Share of fossil carbon $x_{F,TC}$: Correlations of values obtained by aBM with values from standardized methods (^{14}C-Method, SDM, MS); results of all RDF samples investigated are considered.

regression between MS and aBM is rather poor, with slope and intercept far off the ideal curve. The high intercept for the MS regression curve of RDF MSW + C&I, together with a relatively clear relationship (R^2 = 0.64), indicates that there is a systematic underestimation of the fossil carbon content by MS when compared to aBM results. This is in agreement with findings in van Dijk & Steketee (2002) [49] where on average almost 20 wt% of biomass are found in the sorted fossil fraction of 10 different RDFs.

Concluding from the separate regression curves per RDF, it has to be considered that especially for RDF C&I and RDF MSW + C&I, only a very limited number of data points are compared (between 4 and 6), which are all in a similar range (between 60 and 90% of fossil carbon). Thus, the findings are regarded as qualitative, rather than quantitative trends.

3.3. Fossil CO_2-emissions from RDF

The elemental composition of the RDF (C, H, N, S, O), which is determined when applying the aBM, can be used to estimate the heating value of the RDF by means of empirical equations. This can be regarded as an advantage of the aBM over the standardized methods as no additional analyses to derive the heating value are necessary. CO_2-emission factors (specific fossil CO_2-emissions) related to the energy content of the RDF can easily be derived and are presented in Table 9 for each RDF investigated. Table 9 additionally provides the specific fossil CO_2-emissions related to the mass, which is derivable from the share of fossil carbon and the total carbon content in the RDF.

The results show that the fossil CO_2 emitted per GJ of heating value ranges from 48 to 71 kg. The fossil CO_2-emission factor related to the mass reveal that 650–1,800 kg fossil CO_2 are emitted per ton of RDF. The lowest fossil CO_2-emission factor is found for Paper Reject, which holds significantly higher water content (around 42 wt%) compared to the other RDFs. The slightly lower water content for RDF C&I (around 5 wt%) compared to RDF MSW + C&I (around 10 wt%) leads to a difference in heating value of around 3 MJ/kg between the two RDFs. Thus, this difference in heating value explains the slightly lower energy-based CO_2-emission factor for RDF C&I compared to RDF MSW + C&I. The difference between these two RDFs is less pronounced and even shows an adverse tendency when the mass-related CO_2-emission factor is regarded. Thus, a distinction between these RDFs is not possible in terms of climate relevance when merely the mass-related emission factor is determined.

4. Conclusions

The study shows that the values obtained by the adapted Balance Method (aBM) are in excellent agreement with the results of the Radiocarbon Method (^{14}C-Method). Mean deviations of –0.9 to +1.9% abs for the share of fossil carbon are found which are statistically insignificant. Thus, the aBM is the only method for which low deviations and good correlations with the results of ^{14}C-Method could be observed for all RDFs investigated. This confirms recent validation results of the aBM [23] (considering that the ^{14}C-Method has the highest analytical precision and lowest uncertainty amongst the available standardized methods for determining the fossil content in RDFs). For the other two methods – Selective Dissolution Method (SDM) and Manual Sorting (MS) – the results of at least one type of RDF are in a range far off the values of the ^{14}C-Method. The reliability of these standardized methods appears to strongly depend on the composition of the RDF analyzed. High trueness and reliability of the aBM results is expected, independent of the RDF type.

Table 9
Fossil CO_2-emission factors determined for the RDFs based on the adapted Balance Method.

	CO_2-Emission factor ($kgCO_{2,fos}$/GJ[1])	CO_2-Emission factor ($kgCO_{2,fos}$/t)	Water content (wt%)	Lower heating value[1] (MJ/kg)
Paper Reject	48 ± 3	650 ± 20	42.0 ± 3.8	13.5 ± 0.3
RDF C&I	66 ± 3	1,800 ± 20	5.1 ± 0.2	27.0 ± 0.9
RDF MSW + C&I	71 ± 3	1,700 ± 20	10.4 ± 0.4	24.1 ± 0.8

[1] The lower heating value is estimated by means of the empirical equation of Boie in Kost (2001) [34].

By applying the SDM, underestimations (although not consistent between the samples) of the fossil carbon share ($x_{F,TC}$) are expected, depending on the RDF type (within this study between −19 and −2% abs). In contrast, the results of MS when applied according to EN 15440:2011 tends to overestimate the share of fossil carbon (within this study up to +14%abs). Furthermore, significant limitations regarding the reliability of SDM and MS results are indicated for certain types of RDFs. Errors are especially introduced into SDM results for the RDF produced out of pre-processed municipal solid waste and commercial and industrial waste (RDF MSW + C&I). Significant shares of fossil materials which dissolve during selective dissolution are thus misleadingly accounted for as biogenic matter. Besides the fact that the results of manual sorting are prone to human error, MS does not appear practical, particularly for RDF with a high share of “mixed” compounds (mix of biogenic and fossil constituents). The biogenic share in mixed compounds such as the fine fraction, textiles, and rubber apparently yields false estimates when using the defined values given in the standard EN 15440:2011.

A critical factor for the application of the aBM is the choice of the necessary input values – the water-and-ash-free elemental composition of the biogenic and the fossil organic matter (TOX_{BIO} and TOX_{FOS}). These values are ideally generated specifically for an RDF by means of initial manual sorting and analyses. However, the study shows that the TOX_{BIO} and TOX_{FOS} values derived for 3 different RDFs are in a close range and similar to values collected in Fellner et al. (2011) [24], as typical values for RDFs processed from household and commercial waste. Considering also the recent findings in Schwarzböck et al. (2017) [36], where TOX_{BIO} and TOX_{FOS} are appraised for 6 different RDFs, it can be assumed that TOX_{BIO} can easily be derived, also without extensive sorting analyses. For the determination of TOX_{FOS}, the oxygen content (TOO) appears to be the parameter which varies the most between different RDFs. Thus, the presence of polymers with comparably high oxygen contents (e.g. polyamide, polyethylene terephthalate, or polyurethane) might limit the universal applicability of TOX_{FOS} values from the literature. The share of these polymers, however, is typically low for RDF produced out of commercial and industrial waste [36,48,50,51]. The generation of RDF-specific input values for the aBM is regarded as important when no information on the origin of the RDF is available or when a low uncertainty of the results (< 3% rel.) is required. Workload could be saved once a database is established where data about different types of RDFs are collected (e.g. on a national basis).

Concerning the viability and costs, the aBM is regarded as competitive with the SDM (which is the method currently most often applied). When the fossil or biogenic content in RDFs is to be determined routinely, the aBM might even be superior to the SDM (faster, less chemicals needed). The ^{14}C-Method provides reliable results, but compared to the aBM generates significantly higher costs and can only be conducted by a limited number of laboratories [52]. Additionally, the choice of the necessary ^{14}C-reference value can be challenging when the age of the biomass is unknown [29,28]. MS is hardly feasible for routine application due to the high workload involved. Within this study, significant inaccuracies are also identified when MS is applied. This confirms that the aBM is the more cost-efficient and reliable approach compared to MS.

The study demonstrates that the developed method is a valid

alternative to standardized methods for determining the fossil and biogenic share in solid RDFs. This confirms and rounds up the previous findings when defined RDF mixtures were investigated by the authors [23,24]. The mass share as well as the share of fossil carbon (which also corresponds to the share of fossil CO_2-emissions from RDF utilization) can readily be derived by analyses of the elemental composition of the RDF and a set of balance equations. Furthermore, the aBM can be applied to determine different other parameters, such as the share of renewable energy or fossil CO_2-emission factors, all of which can be derived without additional analyses required.

Further investigations will focus on possible simplifications of the method, in particular regarding the generation of the necessary input data (TOX_{BIO} and TOX_{FOS}).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2017.12.076.

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